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ON STABILITY OF FRUSTRATED QUANTUM MAGNETIC STATES IN FULLERENES

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Gutzwiller variational ground states $|\Phi^G\rangle$ of π electrons, described by single-band half-filling Hubbard model, were determined for the molecules C_{60} and C_{70} and their energies and magnetic properties investigated. To construct these states two types of trial functions were used: generalized spin-density wave $|\Phi_{SD}\rangle$ and tight-binding wave $|\Phi_{TB}\rangle$. Our results evidently show that the Gutzwiller state $|\Phi_{TB}^G\rangle$ determined by means of function $|\Phi_{TB}\rangle$ has lower energy than the other investigated variational states $|\Phi_{SD}^G\rangle$. Mean values of the operators in the Gutzwiller states were calculated using Monte Carlo method.

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1. Introduction

It is commonly known that, because of presence of pentagons in fullerenes the magnetic ground state of π electrons (taken in strong Coulomb repulsion approximation) is frustrated and nontrivial [1, 2]. On the other hand, it is known that hopping integral t and Coulomb repulsion U are of the same order in the molecules C_N . Exact value of these parameters is unknown, but the intermediate values $U/t \approx 3-5$ in Hubbard Hamiltonian may be realistic.

Thus, the problem of stability of frustrated magnetic states in the latter case deserves a closer investigation. We investigate this problem assuming that variational Gutzwiller state is a good approximation of the ground state of the C_N molecules. It is defined as $|\Phi^G\rangle = \prod_i (1 - g_i n_{i\uparrow} n_{i\downarrow}) |\Phi\rangle$, where $|\Phi\rangle$ is a trial state, $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$ and $c_{i\sigma}^\dagger$, $c_{i\sigma}$ are the fermion operators, index i runs over all carbon atoms in C_N and σ is a spin label. Variational parameters $g_i = g$, $i = 1, \dots, N$ are determined from minimum of total energy $E(g) = \langle \Phi^G | H | \Phi^G \rangle / \|\Phi^G\|^2$, where

$$H = \sum_{\langle i,j \rangle, \sigma, \sigma'} t_{i\sigma, j\sigma'} c_{i\sigma}^\dagger c_{j\sigma'} + U \sum_i n_{i\uparrow} n_{i\downarrow} \quad (1)$$

is the C_N molecule's Hubbard Hamiltonian.

2. Determination of the electronic ground states

We chose N -electron (half-filling) product state (Slater state) of the lowest energy, obtained from single-particle states of kinetic energy $T = \sum_{(i,j),\sigma,\sigma'} t_{i\sigma,j\sigma'} \times c_{i\sigma}^\dagger c_{j\sigma'}$ as our trial state. We consider two types of those states:

(i) Tight-binding (TB) state $|\Phi_{\text{TB}}\rangle$, when $t_{i\sigma,j\sigma'} = t_{i,j}\delta_{\sigma,\sigma'}$, $t_{i,j}$ is different from zero and equal to t only for the nearest neighbors i, j in C_N molecule.

(ii) Generalized spin-density-wave (SD) state $|\Phi_{\text{SD}}\rangle$, when the kinetic interactions $t_{i\sigma,j\sigma'}$ are chosen in agreement with local spin quantization axes, imposed by magnetic ground state of the C_N molecule.

This magnetic state can be obtained from energy minimum of classical Heisenberg Hamiltonian (cf. [1, 2]), which corresponds to the situation where in Hamiltonian (1) ($t_{i\sigma,j\sigma'} = t_{i,j}\delta_{\sigma,\sigma'}$) we first take the limit $U \rightarrow \infty$ and then the classical limit. Directions of local axes are imposed on each i -th carbon atom by equilibrium orientation of i -th spin i.e. by two spherical angles θ_i and ϕ_i . It can be shown that $t_{i\sigma,j\sigma'} = t_{ij}(R_i^\dagger R_j)_{\sigma\sigma'}$, where R_i is a $SU(2)$ matrix which rotates initial axes of quantization (corresponding to Hamiltonian TB) in the direction imposed by angles θ_i and ϕ_i .

There are three isomers of the C_{60} molecule with symmetry groups D_{2h} (or T_h), D_{3d} and D_{5d} . Number of different magnetic ground states for the isomers is equal respectively to 2, 3, 2 [3]. Since the differences between those states are very small we take for our calculations two states $|\Phi_{\text{SD}}^1\rangle$ and $|\Phi_{\text{SD}}^2\rangle$ corresponding to magnetic valleys of D_{2h} (or T_h) isomer. The C_{70} molecule has one isomer, which can be in 3 different ground states corresponding to three different states of SD Hamiltonian (1).

In our investigation of the states $|\Phi_{\text{TB}}^G\rangle$ and $|\Phi_{\text{SD}}^G\rangle$ properties we calculated functions $E(g)$ as well as mean values of other operators like $M_z = n_{i\uparrow}$, $M_{zz}^{++} = n_{i\uparrow}n_{j\uparrow}$, $M_{zz}^{+-} = n_{i\uparrow}n_{j\downarrow}$, where the indices i, j belong to pentagon within C_N molecule and are the nearest neighbors.

We proceeded as follows. First we calculated functions $E(g)$, in the interval $0 \leq g \leq 1$ for chosen ratio U/t and state $|\Phi^G\rangle$ — the minimum of that function corresponds to variational parameter g^* . Then in the state $|\Phi^G(g^*)\rangle$ we calculated the energy $E(g^*)$ and mean values of the operators M_z , M_{zz}^{++} , M_{zz}^{+-} . All the mean values in the Gutzwiller state were calculated using the Monte Carlo method described in [4].

3. Results

The results of calculations for the molecule C_{60} are shown in Figs. 1 and 2. Figure 1 shows that variational state $|\Phi_{\text{TB}}^G\rangle$ has clearly lower energy than the $|\Phi_{\text{SD}}^{G,1}\rangle$ and $|\Phi_{\text{SD}}^{G,2}\rangle$ states. This is exactly the opposite to the result obtained by [5] in analogous calculations carried out for Hartree-Fock (HF) approximation: energy of the state $|\Phi_{\text{TB}}^{\text{HF}}\rangle$ is higher (starting from a critical value of parameter $(U/t)_c \approx 2.7$) than the energies of $|\Phi_{\text{SD}}^{\text{HF},\alpha}\rangle$, $\alpha = 1, 2$ states. We think that this can be explained by the fact that absolute value of correlation energy is lowered in the $|\Phi_{\text{TB}}^{\text{HF}}\rangle$ state while in the $|\Phi_{\text{SD}}^{\text{HF},\alpha}\rangle$ states it is partly correctly taken into account.

The variational Gutzwiller state seems to be better suited for the description of short-range electron correlations in C_{60} molecule. Figure 2 shows that in energet-

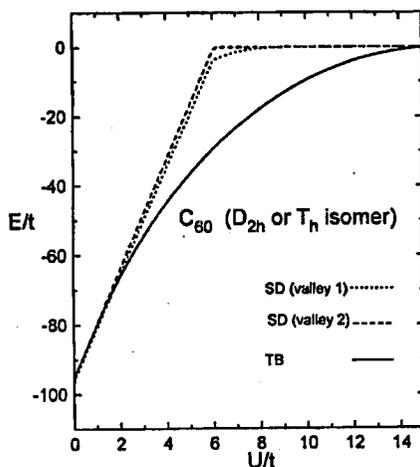


Fig. 1. Dependence of C_{60} molecule electron ground state energy E (half-filled band) in the Gutzwiller variational state on the Coulomb repulsion energy U , t — hopping integral. Continuous line corresponds to stable state (of the lowest energy) $|\Phi_{TB}^G\rangle$. The two remaining lines correspond to unstable variational states $|\Phi_{SD}^{G,\alpha}\rangle$, $\alpha = 1, 2$.

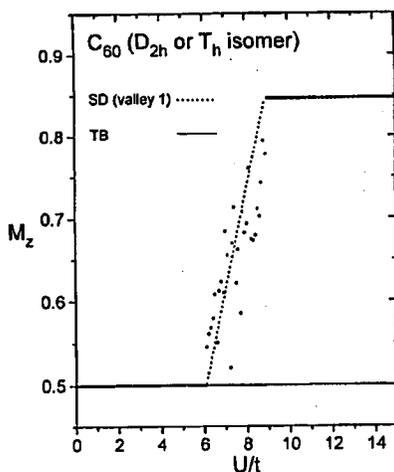


Fig. 2. Mean value $M_z = \langle n_{i\uparrow} \rangle_G$ in the Gutzwiller variational ground state of the C_{60} molecule as a function U/t . The horizontal continuous line $M_z = 0.5$ corresponds to stable state $|\Phi_{TB}^G\rangle$. The stair-like line corresponds to unstable variational state $|\Phi_{SD}^{G,1}\rangle$. Square dots denote Monte Carlo calculations results, dashed line denotes line fitting. For analogous graph for unstable state $|\Phi_{SD}^{G,2}\rangle$ the stair-like line is even more clearly visible.

ically more stable solution we get $M_z = \langle n_{i\uparrow} \rangle_G = 0.5$, which corresponds to the situation when there is no distinguished spin direction on the carbon atoms. This picture shows also that in the less stable states $|\Phi_{SD}^{G,\alpha}\rangle$, starting from a critical value of $(U/t)'_c \approx 6.1$ we get $M_z > 0.5$, this means that the local spin quantization axes are subjected to smaller fluctuations in surrounding of classical directions θ_i and ϕ_i . This result, despite the fact that it is energetically instable, is in agreement with analogous result for the states $|\Phi_{SD}^{HF,\alpha}\rangle$, but in this case $(U/t)_c \approx 2.7$ (cf. [5]).

Antiferromagnetic type of correlations should increase with the growth of the ratio U/t in C_{60} . This is exactly the case. The mean values of operators M_{zz}^{+-} and M_{zz}^{++} calculated in the state $|\Phi_{TB}^G\rangle$ tend respectively to ≈ 0.3 and ≈ 0.15 . In case of the C_{70} molecule we obtained the same results as for the C_{60} i.e. energetically more stable is the $|\Phi_{TB}^G\rangle$ state than the $|\Phi_{SD}^G\rangle$ states. Critical value of the $(U/t)'_c$ is also ≈ 6.1 . We expect that the ground state of all higher neutral (not ionized) fullerenes C_N will have similar properties. In real molecules $U/t \approx 3-5$ therefore the antiferromagnetic correlations in C_N are weak. The π electrons behave like weakly antiferromagnetically correlated spin liquid. The properties of ground state of crystal consisting of C_N molecules remain an open question.

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References

- [1] D. Coffey, S. Trugman, *Phys. Rev. Lett.* **69**, 176 (1992).
- [2] A. Koper, J. Stankowski, M. Thomas, *Acta Phys. Pol. A* **85**, 351 (1994).
- [3] A. Koper, M. Mucha, to be published.
- [4] A. Koper, M. Mucha, *Acta Phys. Pol. A* **91**, 391 (1997).
- [5] L. Bergomi, J.P. Blaizot, Th. Jolicoeur, E. Dagotto, *Phys. Rev. B* **47**, 5539 (1993).